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SUBJECT DIELECTRIC CONSTANT OF HYDROGEN		NAME R. J. Corruccini		
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Data on the dielectric constant of hydrogen in all phases have been presented in a compendium¹ by the CEL Data Center. The compendium presents the original data from seventeen references as measured under various conditions of temperature and pressure. One who wishes to derive from this source the dielectric constant of hydrogen in a particular condition faces some perplexing problems:

(1) It is not apparent which of the data are to be preferred on grounds of accuracy. (2) It is not indicated how one should interpolate or extrapolate, if this should be necessary. (3) It is not indicated how one can reduce the various data to some common basis for comparison and correlation. The purpose of this note is to show how the Clausius-Mosotti equation can be used to accomplish all of the above ends.

The C-M equation can be found in most textbooks of physical chemistry. It is derived from classical electrostatic theory on the assumptions that the molecules are non-polar and spherical, there are no short-range interactions between them, and their spatial distribution is isotropic.^{2,3} Hydrogen satisfies only the first assumption. However, errors due to the other assumptions tend to vanish as the density decreases⁴ and are negligible for non-polar gases at ordinary pressures. Kirkwood⁴ has developed a more complete theory that is valid up to moderate densities, but there is no quantitative theory that is generally applicable at densities characteristic of liquids.

The C-M equation is as follows:

$$\frac{\epsilon - 1}{\epsilon + 2} v = p$$

in which

ϵ is the dielectric constant

v is the specific volume

p is the specific polarization, a property of the substance having the same dimensions as v .

The corresponding molar quantity, P , often is used. Similarly a molecular parameter, a , the "polarizability" can be identified. It is given by

$$P = \frac{4}{3} \pi N a$$

where N is Avogadro's number. The polarizability is the mean moment induced in a molecule by unit homogeneous electric field. To the extent that p , P , or a is a constant for a given substance, the substance may be said to obey the C-M equation.

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Now in applying the C-M equation to non-polar liquids, deviations certainly are to be expected due to violation of all of the assumptions previously stated except the first. However, it is found that the deviations are never large and, hence, the equation remains useful as a device for correlating data. In this application, the polarization parameters play a role like that of the compressibility factor in correlating P-V-T behavior. In fact, for hydrogen it will be shown that all of the available data can be represented within the probable experimental errors by a single value of the polarization, even though they cover a thousandfold range of densities.

Now the available experimental data will be examined.

Liquid hydrogen. The CEL compendium¹ gives four references, of which three are from Leiden. A reading of the most recent of the three (Werner & Keesom, 1925) and examination of the scatter of the ϵ and p values shows clearly that the earlier two (by Breit & Onnes, 1924 and Wolfke & Onnes, 1924) now should be given no weight. The fourth reference (Guillien, 1940) appears to be comparable in precision and accuracy to Werner & Keesom. Both papers cover the range, 14-20.4°K and the authors conclude that their data show no consistent variations in p that could be interpreted as deviations from the C-M equation. To these should be added a value at the boiling point by van Itterbeek & Spaepen⁵ of apparently comparable reliability. Mean values of p obtained in these investigations are given in table 1.

In addition it is possible to compute the dielectric constant from refractive index data using the relation, $\epsilon = n_{\infty}^2$, where n_{∞} is the refractive index extrapolated to very long wavelengths. Johns & Wilhelm⁶ have measured the refractive index of liquid hydrogen from 14° to 20.4°K at wavelengths in the visible. Guillien has calculated the value $n_{\infty}^2 = 1.2288 \pm .0003$ at 20.4°, from their data. The corresponding value of p calculated using the specific volume given in RP1932² is shown in table 1.

Two compilations have been published giving "best" values for liquid hydrogen.⁷ Friedman used the data of Wolfke & Onnes rather than those of Werner & Keesom in choosing a value of p . Maryott & Smith⁸, who give a best value for ϵ at 20.4°K, also used the data of Wolfke & Onnes. Consequently, the p and ϵ values recommended by these compilers are regarded as too low.

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Solid hydrogen. The data of Werner & Keesom disagree violently with those of Guillien. From experiences at CEL⁹ with liquid and solid nitrogen, it is clear that discrepancies of this kind readily occur due to the difficulty of ensuring that the solid, which has to be cast in place in the measuring condenser, actually has its theoretical density and is free from voids. In order to obtain a meaningful test of the C-M equation using a solid, extreme care must be taken with the preparation of the sample, or else its density must be determined in place by an independent method.

Gaseous hydrogen. The CEL compilation¹ and the Landolt-Börnstein tables¹⁰ between them provide a score of references to direct measurements of the dielectric constant. Neither provides a critical selection. On the other hand, Maryott & Buckley¹¹ have provided a "best" value of ϵ at 20°C and 1 atmosphere. However, it is based entirely on optical and microwave measurements of the refractive index using the relation, $\epsilon = n_{\infty}^2$. Maryott and Buckley dismiss the direct measurements of ϵ with this statement: "In a majority of cases, values of the dielectric constant measured at radio frequencies do not appear to be of sufficient accuracy to provide useful information for reference purposes." A full treatment of the dielectric behavior of hydrogen would make use of refractive index data on the compressed gas also. Lacking a ready-to-hand compilation of refractive index data, this will not be attempted here. A value of p calculated from Maryott and Buckley's recommended dielectric constant using the specific volume of the real gas¹² is presented in table 1.

Of special interest to this inquiry are those few studies of the dielectric constant that cover wide ranges of temperature, pressure and density. The extremes of temperature are represented by van Itterbeek and Spaepen¹³ (20° - 291°K) and Forro¹⁴ (295° - 571°K). These authors obtained constant values of p within their experimental limits of accuracy. A more rigorous test is provided by the data of Michels, Sanders and Schipper¹⁵ at 25°C and 100°C and at pressures from 1 to 1425 atm. The maximum density achieved equals that of saturated liquid at 26°K. In spite of the great range of densities covered by Michels, the polarization showed no discernible trend with density or temperature. His average value is included in table 1.

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Summary. The following table summarizes the experimental results that are regarded as especially significant. None of the investigators referred to the matter of ortho-para composition, and so it is assumed that the samples were normal hydrogen in all cases.

Table 1
Specific Polarization of Hydrogen

Reference	State	Temperature Range	Approx. Range of Specific Volume	p
		°K	cc/g.	cc/g.
Werner & Keesom 1925	Liq.	14 - 20.4	13-14	1.010 ± .002
Guillien 1940	Liq.	14 - 20.4	13-14	0.9984 ± .002
Van Itterbeek & Spaepen 1942	Liq.	20.4	14	0.988 ± .003
Johns & Wilhelm 1937	Liq.	20.4	14	*0.9986 ± .001
Maryott & Buckley 1953	Gas	~293	12,000	*1.0104 ± .001
Michels, et al 1953	Gas	298, 373	16-11,000	1.001 ± .002

* From measurements of refractive index.

Inasmuch as none of the researches showed internal evidence of dependence of p upon the experimental conditions, the variations in p shown above cannot be construed as evidence for deviations from the C-M equation. Parts of the discrepancies may be attributed to the use of different data for the specific volumes and to accidental variations in ortho-para composition. However, the discrepancies are too large to be fully accounted for in these ways, and in large part must be charged to undisclosed systematic errors in the experiments.

A value of p equal to 1.00 cc/g. is seen to represent all of the selected investigations within ±1%. This uncertainty corresponds to about ±0.2% in the dielectric constant of the liquid. The above value is tentatively recommended for use in calculations, although there are some rather tenuous reasons for favoring a higher value. Since, from the C-M equation

$$\epsilon = \frac{v + 2p}{v - p}$$

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then, if p for hydrogen is taken to be exactly one, $\epsilon = \frac{v+2}{v-1}$. A future note will present a table of provisional values of ϵ calculated in this way.

The degree of constancy of polarization that has been demonstrated for hydrogen is rather exceptional. Böttcher² (p. 209) attributes this to hydrogen having an exceptionally small value of the imperfection parameter, a/a^3 , where a is the average molecular radius. Conversely, this parameter is larger for CO_2 , and the polarization of this gas has been found to vary with pressure by about 2% in 150 atm. Böttcher's interpretation is based upon his own formula for the deviation from the C-M equation due to short-range electrostatic interactions. However his formula shows that this deviation depends upon ϵ and, hence, a as well as upon a/a^3 . Values of these quantities for some cryogenic substances are shown in table 2. The values of a are seen to be more markedly different than are the values of a/a^3 , but both trend in such a way as to suggest that N_2 and O_2 will show relative deviations from the C-M equation intermediate between those of H_2 and CO_2 while He should show even less deviation than H_2 .

Table 2
Imperfection Parameters

Substance	P	$10^{24} a$	$*a$	a/a^3
	cc/mol	cc	\AA°	
He	0.51	0.20	1.28	0.10
H_2	2.02	0.79	1.47	0.25
N_2	4.3	1.71	1.85	0.27
O_2	4.0	1.59	1.76	0.29
CO_2	7.3	2.89	2.1	0.31

*Based on a collection¹⁶ of values determined from second virial coefficients and viscosities. The former were given extra weight.

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